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(54) Title: GROUP 11 TRANSITION METAL AMINE CATALYSTS FOR OLEFIN POLYMERIZATION

(57) Abstract

A catalyst composition comprising a catalyst and an activating cocatalyst is claimed. The catalyst has the formula LMX_1X_2, wherein X_1 and X_2 are independently halide, hydride, triflate, acetate, trifluroacetate, tris perfluorotetraphenyl borate, tetrafluoroborate, straight chain or branched alkyl or alkoxy of 1-12 carbon atoms, cycloalkyl or cycloalkoxy of 3-12 carbon atoms, or aryl; M is Cu, Ag, or Au; L is a nitrogen-containing bidentate ligand. The nitrogen in L is preferably contained in 5 or 6-membered heterocyclic rings, two of which are bonded to a hydrocarbyl bridging group. The activating cocatalyst is generally an aluminum compound or other Lewis acid.

GROUP 11 TRANSITION METAL AMINE CATALYSTS FOR OLEFIN POLYMERIZATION

FIELD OF THE INVENTION

The invention is directed towards tetrahedral and psuedo-tetrahedral late transition metal polymerization catalyst complexes and their use in forming homopolymers from olefins or polar monomers and copolymers from olefins and polar monomers.

BACKGROUND

Polymers and copolymers may be formed from olefinic monomers by using transition metal metallocene catalyst technology. This well-known technology uses catalysts containing early transition metal atoms such as Ti and Zr.

Even though polyolefins formed by such metallocene catalysts posses enhanced properties over polyolefins produced by conventional Ziegler-Natta catalysts, further improvements in properties such as wettability and adhesiveness may be possible. It is believed that including polar monomers in an olefinic polymer or copolymer would improve wettability and adhesiveness in those materials. Unfortunately, polar monomers tend to poison early transition metal catalysts.

Certain late transition metal complexes of palladium and nickel incorporate some polar monomers. However, such catalyst systems are costly. Also, the polymers so produced are highly branched (85-150 branches/1000 carbon atoms) and the functionalities are not in the chain but at the ends of branches. Consequently, they are limited to polar monomer contents $\leq$ about 15 mol%. Another disadvantage of these systems is that they incorporate only a limited number of polar monomers (e.g. alkyl acrylates and vinyl ketones). Methyl methacrylate and *n*-butyl vinyl ether are mildly inhibiting or inert.

Consequently, there remains a need for a polymerization catalyst capable of forming olefinic polymers and copolymers and that are effective polymerization catalysts in the presence of polar monomers.

SUMMARY OF THE INVENTION

In one embodiment, the invention is a catalyst system comprising:

(a) a catalyst having the formula LM X_1X_2 wherein X_1 and X_2 are independently selected from the group consisting of halogens, hydride, triflate, acetate, triflouroacetate, tris perflourotetraphenyl borate, tetraflouro borate, C1 through C12 straight chain or branched alkyl or alkoxy, C3 through C12 cyclo alkyl or cyclo alkoxy, and aryl; M is selected from the group consisting of Cu, Ag, and Au; and L is a nitrogen-containing bidentate ligand,

and

(b) an activating cocatalyst.

A method is provided for polymerizing an olefinic monomer selected from the group consisting of (a) acyclic aliphatic olefins, (b) olefins having a hydrocarbyl polar functinally and (c) mixtures of (i) at least one olefin having a hydrocarbyl functionality and (ii) at least one acyclic aliphatic olefin, the method comprising contacting the olefin monomer under polymerization conditions with the catalyst system of this invention.

In still another embodiment, the invention is a substantially linear copolymer represented by the formula:

$$-\!\left(A\right)_{1-y}\!\left(CH_2-\underset{\displaystyle X}{\underset{|}{C}}R\right)_y$$

where A is a segment derived from an acyclic aliphatic olefin of 2 to about 20 carbon atoms;
R is H or CH_3;
X is $-OR^1$ or $-COOR^1$;
R^1 is an alkyl group of 1 to 24 carbon atoms; and Y is from about 0.02 to about 0.95

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the structure of Cu(MeBBIOMe)Cl_2.

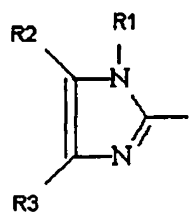
Figure 2 shows the structure of Cu(tribut BBIM) Br_2.

DETAILED DESCRIPTION OF THE INVENTION

The catalyst of this invention is a complex having the formula LM X_1X_2, wherein L is a nitrogen-containing bidentate ligand represented by the formula:

[ABA'] and [AA'],

wherein A and A' are independently selected from the group consisting of



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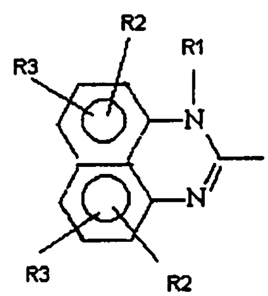

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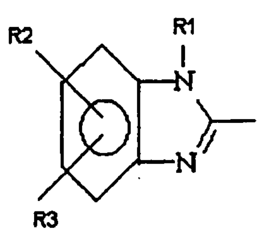

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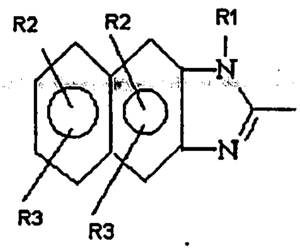


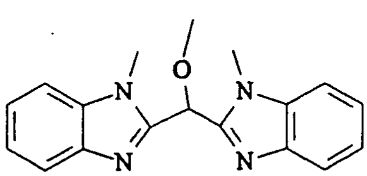
wherein R1 is independently selected from the group consisting of hydrogen, C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl, aryl, and triflouroethane;

R2 and R3 are independently selected from the group consisting of hydrogen, C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl, C1 through C12 alkoxy, F, Cl, SO_3, C1 through C12 perflouroalkyl, and $N(CH_3)_2$;

B is selected from the group consisting of non-substituted C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl; methoxy; amino; halo; and C1 through C12 haloalkyl substituted straight chain or branched alkyl or cyclo alkyl of up to 12 carbon atoms or C1 – C40 aryl or alkylaryl groups.

X_1 and X_2 are independently selected from the group consisting halogens, hydride, triflate, acetate, triflouroacetate, tris (perflourotetraphenyl) borate, and tetraflouro borate, C1 through C12 straight chain or branched alkyl or alkoxy, C3 through C12 cyclo alkyl or cyclo alkoxy, and aryl;

Accordingly, some of the ligands of the present invention have the structures:



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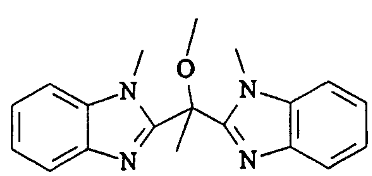
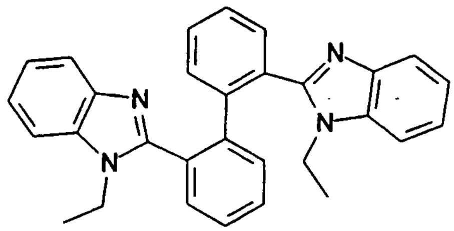
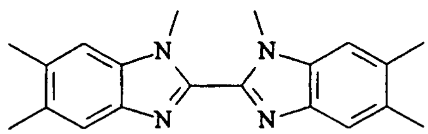
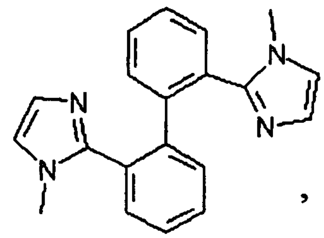
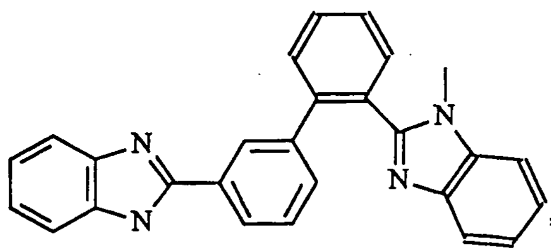
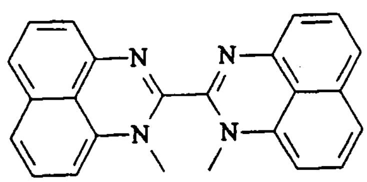


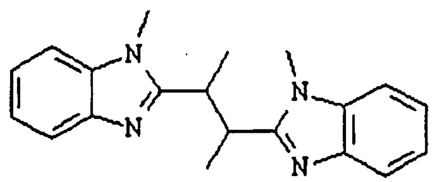


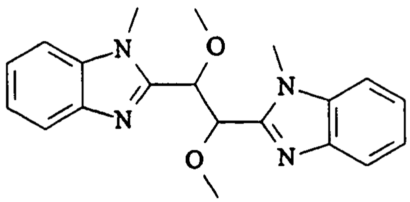
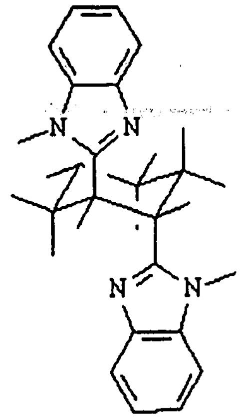
,

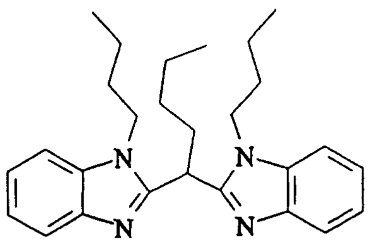
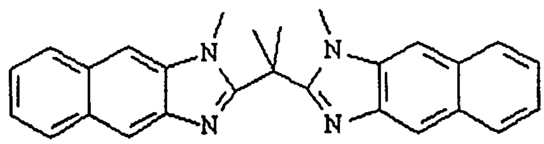
,

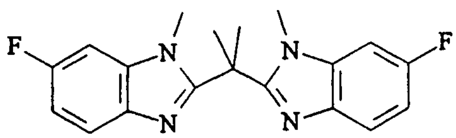
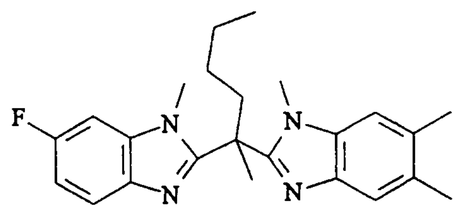
,

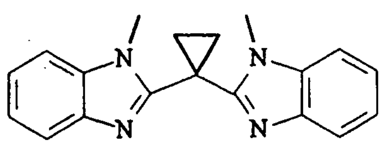
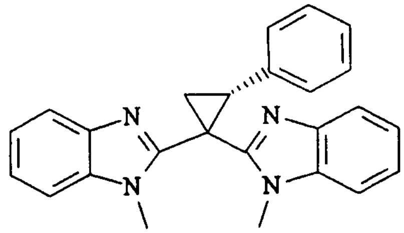
,

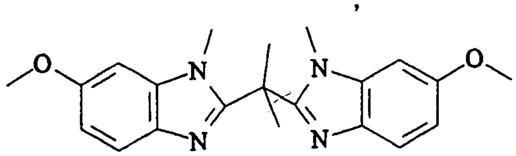
,

, ,

, ,

, ,

, ,

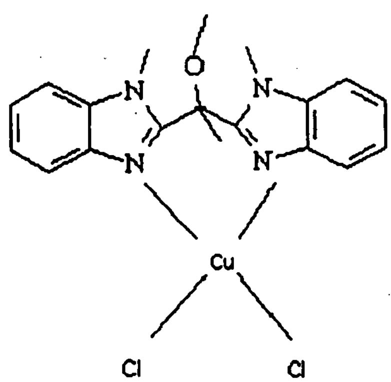
and . For compactness, some bonds are shown without termination; these bonds are terminated by methyl groups.

The metal M is selected from Cu, Ag, and Au. Among Cu, Ag, and Au, Cu is preferred; among X_1 and X_2, halogens are preferred.

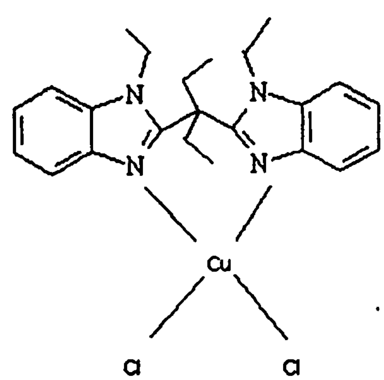
Suitable non-halide X_1 and X_2 include triflate, triflouroacetate, tris perflourotetraphenyl borate, or tetraflouro borate.

Among the catalyst complexes of the present invention, those having the 1, 1' bis(1-methylbenzimidazol-2 yl)1" methoxyethane ligand or the 3,3'(1-ethylbenzimidazol-2yl) pentane ligand, or 2,2' bis[2-(1-alkylbenzimidazol-2yl)] biphenyl, where the alkyl group is from C1-C20, and $X_1 = X_2 =$ chloride are particularly preferred.

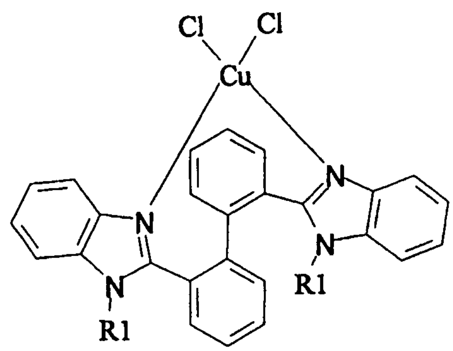
1, 1' bis(1-methylbenzimidazol-2 yl)1" methoxyethane ligands with copper as the metal and chlorine as X_1 and X_2 have the structure



3,3'(1-ethylbenzimidazol-2yl) pentane ligands with copper as the metal and chlorine as X_1 and X_2 have the structure



2,2'bis[2-(1-alkylbenzimidazol-2yl)]biphenyl ligands with copper as the metal and chlorine as X_1 and X_2, and C1-C20 as R_1, have the structure



Advantageously, the catalysts of the present invention are not poisoned by compounds containing hydrocarbyl polar functionalities when used in the formation of polymers and copolymers synthesized all or in part from olefinic monomers. As such, the catalysts of the present invention are useful in preparing polymers and copolymers formed from olefinic monomers, such as polyethylene; polymers and copolymers formed from monomers containing hydrocarbyl polar functionalities such as poly(methyl methacrylate); and copolymers derived from olefins and monomers containing hydrocabyl polar functionalities such as poly (ethylene-co-methyl methacrylate).

Acccording to the present invention, a catalyst having the formula L M X_1X_2, wherein L, M, X_1, and X_2 are as previously defined, is combined with an activating cocatalyst. Examples of such cocatalysts include aluminum compounds containing an Al-O bond such as the alkylalumoxanes such as methylalumoxane ("MAO") and isobutyl modified methylalumoxane; aluminum alkyls; aluminum halides; alkylaluminum halides; Lewis acids other than any of the foregoing list; and mixtures of the foregoing can also be used in conjunction with alkylating agents, such as methyl magnesium chloride and methyl lithium. Examples of such Lewis acids are those compounds corresponding to the formula: $R""_3B$, wherein R"" independently each occurrence is selected from hydrogen, silyl, hydrocarbyl, halohydrocarbyl, alkoxide, aryloxide, amide or combinations thereof, said R"" having up to 30 nonhydrogen atoms.

It is to be appreciated by those skilled in the art, that the above formula for the preferred Lewis acids represents an empirical formula, and that many Lewis acids exist as dimers or higher oligomers in solution or in the solid state. Other Lewis acids which are useful in the catalyst compositions of this invention will be apparent to those skilled in the art.

Other examples of such cocatalysts include salts of group 13 element complexes. These and other examples of suitable cocatalysts and their use in organometallic polymerization are discussed in U. S. Patent No. 5,198,401 and PCT patent documents PCT/US97/10418 and PCT/US96/09764, all incorporated by reference herein.

Preferred activating cocatalysts include trimethylaluminum, triisobutylaluminum, methylalumoxane, ethylalumoxane, chlorodiethyaluminum, dichloroethylaluminum, triethylboron, trimethylboron, triphenylboron and halogenated, especially fluorinated, triphenyl boron compounds.

Most highly preferred activating cocatalysts include triethylaluminum, methylalumoxane, and fluoro-substituted triaryl borons such as tris(4-fluorophenyl)boron, tris(2,4-difluorophenylboron), tris(3,5-bis(trifluoromethylphenyl) boron, tris(pentafluorophenyl) boron, pentafluorophenyl-diphenyl boron, and bis(pentafluorophenyl) phenylboron. Such fluoro-substituted triarylboranes may be readily synthesized according to techniques such as those disclosed in Marks, et al., J. Am. Chem. Soc., 113, 3623-3625 (1991).

The catalyst can be utilized by forming the metal complex LM X_1X_2 and where required combining the activating cocatalyst with the same in a diluent. The preparation may be conducted in the presence of one or more addition polymerizable monomers, if desired. Preferably, the catalysts are prepared at a temperature within the range from -100°C. to 300°C., preferably 0°C to 250°C, most preferably 0°C to 100°C. Suitable solvents include liquid or supercritical gases such as CO_2, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, halogenated hydrocarbons such as chlorobenzene, and dichlorobenzene perfluorinated C_{4-10} alkanes and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-

methyl-1-pentene, 1-octene, 1-decene, and 4-vinycylohexane, (including all isomers alone or in mixtures). Other solvents include anisole, methylchloride, methylene chloride, 2-pyrrolidone and N-methylpyrrolidone. Preferred solvents are aliphatic hydrocarbons and aromatic hydrocarbon, such as toluene.

In the practice of this invention, it is believed that the cocatalyst interacts with the catalyst to create a polymerization-active, metal site in combination with a suitable non-coordinating anion. Such an anion is a poor nucleophile, has a large size (about 4 Angstroms or more), a negative charge that is delocalized over the framework of the anion, and is not a strong reducing or oxidizing agent [S. H. Strauss, Chem. Rev. 93, 927 (1993)]. When the anion is functioning as a suitable non-coordinating anion in the catalyst system, the anion does not transfer an anionic substituent or fragment thereof to any cationic species formed as the result of the reaction.

The equivalent ratio of metal complex to activating cocatalyst (where employed) is preferably in a range from 1:0.5 to $1:10^4$, more preferably from 1:0.75 to $1:10^3$. In most polymerization reactions the equivalent ratio of catalyst:polymerizable compound employed is from 10^{-12}: to 10^{-1}:1, more preferably from 10^{-9}:1 to 10^{-4}:1.

The catalysts of the present invention have a tetrahedral or psuedo-tetrahedral structure. It is believed that this structure is present when the catalyst is in the form of an isolated solid compound and when the catalyst is used in the presence of activating cocatalysts of this invention under homopolymerization or copolymerization conditions.

The structure of Figure 1 will be used to illustrate the tetrahedral and psuedo-tetrahedral structures of this invention and to distinguish those structures from square planar structures. This comparison is for illustration purposes only, and is not intended to be limiting in any way. Figure 1 shows nitrogen atoms N1 and N3 together with metal atom Cu1 describe a tetrahedron with the metal atom at the apex and the nitrogen atoms occupying diagonally opposed positions on a base. Similarly, atoms Cl1 and Cl2 form a tetrahedron with Cu1, the metal atom being at the apex and the chlorines occupying diagonally opposed basal positions. In a perfect tetrahedron, of equal bond lengths, the included angles transcribing N1-Cu1-Cl1, Cl2-Cu1-Cl1, N3-Cu1-Cl1, and N1-Cu1-Cl2 would all be about 109°. In psuedo-tetrahedral structures, these angles deviate from 109°. Both structures are readily distinguishable from square planar structures, wherein the metal atom lies in the same plane as the chlorines and nitrogens.

Olefinic monomers useful in the forming homo and copolymers with the catalyst of the invention include, for example, ethylenically unsaturated monomers, nonconjugated dienes, and oligomers, and higher molecular weight, vinyl-terminated macromers. Examples include C_{2-20} olefins, vinylcyclohexane, tetrafluoroethylene, and mixtures thereof. Preferred monomers include the C_{2-10} α-olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene or mixtures of the same.

Monomers having hydrocarbyl polar functionalities useful in forming homo and copolymers with the catalyst of the invention, are vinyl ether and C_1 to C_{20} alkyl vinyl ethers such as *n*-butyl vinyl ether, acrylates, such as C1 to C24, or alkyl acrylates such as *t*-butyl acrylate, and lauryl acrylate, as well as methacrylates such as methyl methacrylate.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from -100°C to 250°C preferably 0°C to 250°C, and pressures from atmospheric to 1000 atmospheres (100 Mpa). Suitable polymerization conditions include those known to be useful for metallocene catalyst when activated by aluminum or boron-activated compounds. Suspension, solution, slurry, gas phase or other process condition may be employed if desired. The catalyst may be supported and such supported catalyst may be employed in the polymerizations of this invention. Preferred supports include alumina, silica, and polymeric supports.

The polymerization typically will be conducted in the presence of a solvent. Suitable solvents include those previously described as useful in the preparation of the catalyst. Indeed, the polymerization may be conducted in the same solvent used in preparing the catalyst. Optionally, of course, the catalyst may be separately prepared in one solvent and used in another.

The polymerization will be conducted for a time sufficient to form the polymer and the polymer is recovered by techniques well known in the art and illustrated in the examples hereinafter.

An important feature of the invention is the formation of substantially linear copolymers having the formula

$$-\!\left(A\right)_{1-y}\!\left(CH_2-\underset{\displaystyle X}{\overset{|}{C}}R\right)_{y}\!-$$

where A is a segment derived from an acyclic aliphatic olefin of 2 to about about 20 carbon atoms; R is H or CH_3; x is $^{\cdot}OR^1$ or $^{\cdot}COOR^1$; R^1 is an alkyl group of 1 to 24 carbon atoms and y is from about 0.02 to about 0.95 and preferrably y is from about 0.18 to about 0.85.

These copolymers have polar functional monomer segments, $-\!\left(CH_2-\underset{X}{C}R\right)\!-$ which are substantially in the chain rather than at ends of branches.

In the case where -A- is a polymer segment derived from ethylene, the branch content of which is below about 20 branches/1000 carbon atoms, for example from about 0.5 to less than 20 branches.

The invention is further described in the following non-limiting examples.

EXAMPLES

I. CATALYST PREPARATION

Example 1 - Preparation of 1,1'bis(1-hydrobenzimidazol-2yl)carbinol (HBBIOH)

A mixture of 8.0 g of (66.6 mmol) of hydroxypropanedioic acid and 14.41 g (133.3 mmol) of 1,2-phenylenediamine in 90 mL of 4 N hydrochloric acid was refluxed for 18 h. The reaction mixture was cooled and the pH was adjusted to about 8 with ammonium hydroxide to give a pale-green solid. The solid was collected by filtration and dried in a vacuum oven to give 8.85 g of 1,1'bis(1-hydrobenzimidazol-2yl)carbinol. Yield : (50.3%); mp 238 °C (subl); ^1H NMR (500 MHz, d^6 DMSO) δ 7.50 (m, 4 H), 7.15 (m, 4 H), 4.70 (s, 1 H), 2.55 (s, 1H). In these examples, NMR resonances are identified as "m" for multiplet and "s" for singlet. IR absorbtions are denoted s for strong, m for medium, and w for weak.

Example 2 - Preparation of 1,1'bis(1-methylbenzimidazol-2yl)1" methoxyethane (MeBBIOMe)

A 1.0 g (3.8 mmol) quantity of HBBIOH was suspended in 50 ml of dry THF. Under Ar, sodium hydride (80% disperssion in mineral oil, 0.68 g, 22.8 mmol) was added to the suspension and was stirred for 0.5 h. A 2.16 g (15.2 mmol) quantity of iodomethane was added dropwise and allowed to stir for 18 h. The reaction mixture was quenched with saturated aqueous sodium sulfate solution. THF was removed by rotory-evaporation. The oil was washed with water and seperated with methylene chloride followed by chromatography. The 1,1'bis(1-methylbenzimidazol-2yl)1" methoxyethane was recrystallized from a mixture of 2-propanol and cyclohexane to give 0.23 g of solid. Yield 18.9% ; mp 194-195 °C; EI-MS 320; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H), 3.27 (s, 3H), 3.67 (s, 6H), 7.26-7.36 (m, 6H), 7.79-7.82 (m, 2H).

Example 3 - Preparation of Cu(MeBBIOMe)Cl_2

A solution of ethanol and triethylorthoformate was prepared by refluxing 30 ml of 100% ethanol and 4 ml of triethylorthoformate. A 245 mg (1.82 mmol) quantity of $CuCl_2$ (99.999% Aldrich) was dissolved in the ethanol/triethylorthoformate solution to form a yellow-green solution. After the addition of 584 mg (1.82 mmol) of solid MeBBIOMe an intensely yellow colored crystalline precipitate formed. The complex, [1,1'bis(1-methylbenzimidazol-2yl)1"methoxyethane]copper(II) dichloride, Cu(MeBBIOMe)Cl_2, was collected by filtration and dried under vacuum. Measurements revealed a melting point (mp) 262-263 °C (decomposition). Elemental analysis calculations predicted relative concentrations of C, 50.19 wt %; H, 4.40 wt %; Cl, 15.61 wt %; and Cu, 14.00 Wt %. Laboratory measurements found C, 50.11 wt %; H, 4.48 wt %; Cl, 15.87 wt %; and Cu, 14.1 wt %; The X-ray crystallographic structure is shown in Fig. 1; bond angles are N3-Cu1-Cl2 101.7°, N1-Cu1-Cl1 104.6°, Cl2-Cu1-Cl1 105.9°, N3-Cu1-Cl1 126.3°, N1-Cu1-Cl2 129.6°. Accordingly, this compound has a psuedo-tetrahedral structure.

Example 4 - Preparation of Cu(tributBBIM)Br_2

A 260 mg (1.16 mmol) quantity of $CuBr_2$ (99.99% Aldrich) was dissolved in 25 mL of ethanol to form an orange-brown solution. After the addition of 365 mg (0.88 mmol) of solid 1,1'bis(1-butylbenzimidazol-2yl)pentane, (tributBBIM), prepared by the methods of Examples 1 and 2, using malonic acid, 1,2-phenylene diamine and butyl iodide as the alkylating agent, a red-brown solution formed. Then 1 mL of triethylorthoformate was added to the soultion and filtered. Upon standing the complex, [1,1'bis(1-butylbenzimidazol-2yl)pentane]copper(II) dibromide, Cu(tributBBIM)Br_2, formed as long thin red prisms. The crystals were collected by filtration and air dried, mp 215 °C (decomp.). The X-ray crystallographic structure is shown in Fig. 2; bond angles were measured to be Br1-Cu1-N11 130.6°, N1-Cu1-Br1 106.4°, N11-Cu1-Br2 99.1°, Br1-Cu1-Br2 100.5°, N1-Cu1-Br2 134.8°. Accordingly, this structure has a psuedo-tetrahedral structure.

Example 5 - Preparation of [3,3'(1-ethylbenzimidazol-2yl)pentane]copper(II) dichloride, Cu(tetEtBBIM)C_{12} and ditrifluoromethylsulfonate, Cu(tetEtBBIM)$(trif)_2$

3,3′ (1-Ethylbenzimidazol-2yl) pentane copper (II) dichloride, Cu(tetEtBBIM)C_{12} was prepared by the Examples 1-3, using malonic acid and 1,2 phenylene diamine and ethyl iodide as the alkylating agent. A suspension of 65 mg of [3,3'(1-ethylbenzimidazol-2yl)pentane]copper(II) dichloride, Cu(tetEtBBIM)Cl_2, was prepared in a solution consisting of 35 ml of methylene chloride and 0.5 ml of triethylorthoformate. To the stirred suspension 67.5 mg of silver trifluoromethylsulfonate, Ag(trif), was added. After stirring about 15 minutes the solution was filtered. After slow evaporation, the filtrate afforded bright blue prisms of Cu(tetEtBBIM)$(trif)_2$ which were collected by filtration. X-ray crystallographic data revealed a = 9.8303 Å, b = 10.3048 Å, c = 16.1909 Å, α = 80.3697°, β = 72.7137°, γ = 71.4988°, Volume = 1480.29 $Å^3$.

Example 6 - Preparation of 2,2′ bis[2-(1-ethylbenzimidazol-2yl]biphenyl] copper(II), Cu(diEtBBIL)Cl_2

A solution of ethanol and triethylorthoformate was prepared by combining 35 mL of 100% ethanol and 4 mL of triethylorthoformate. A 500 mg (2.93 mmol) quantity of $CuCl_2$-$2H_2O$ (Aldrich) was dissolved to form a green solution. After the addition of 500 mg (1.13 mmol) of solid diEtBBIL, ± 2,2'bis[2-(1-ethylbenzimidazol-2yl)]biphenyl, prepared by the method of Example 1 and 2, using 2,2′-diphenic acid, 1,2-phenylenediamine, and ethyl iodide as alkylating agent, the mixture was refluxed for 5 minutes. Upon cooling an organe-brown microcystalline solid was obtained. The solid was collected by filtration, washed with triethylorthoformate and pentane, then air dried to give 585 mg of orange-brown solid; mp 206-207°C (decomp). The orange-brown solid was recrystallized from hot nitromethane to give the yellow crystalline complex, ± 2,2'-bis[2-(1-ethylbenzimidazol-2yl)]biphenylcopper(II) dichloride, Cu(diEtBBIL)Cl_2, which was collected by filtration and dried under vacuum; mp 275°C (soften) 285°C (decomp.); Anal. Calcd. Cu, 11.01 Found Cu, 11.01; IR(KBr pellet, cm^{-1})3439 br, 3069 w, 2962 w, 1668 s 2947 sh, 2926s, 2852 m, 1465 s, 1418 s, 776 sh, 761 sh, 746 s. X-ray crystallographic data: N1-Cul-N3 111°; P2(1)2(1), Z=4, a=15.980Å, c=20.538 Å, α=90°, γ=90°, Volume = 5387.36 $Å^3$; solution EPR (toluene/nitromethane) A_{11}=15 Gauss.

Example 7 - Preparation of [± 2,2′-bis[2-(1-octylbenzimidazol-2yl)]biphenyl]copper(II) dichloride, Cu(diOctBBIL)Cl_2

A 200 mg quantity of $CuCl_2$•$2H_2O$ (Aldrich) was dissolved in 15 ml of ethanol to give a green solution. Then 100 mg of diOctBBIL, prepared by the method of Example 1 and 2, using 2,2′-diphenic acid, 1,2 phenylenediamine and 1-iodooctane as the alkylating agent, was added as an oil, followed by the addition of 1 ml of triethylorthoformate. The mixture was heated to reflux for 10 min., then allowed to cool. Upon standing the solution afforded bright-yellow thin plates of [± 2,2′-bis[2-(1-octylbenzimidazol-2yl)]biphenyl]copper(II) dichloride. The crystalline solid was collected by filtration and washed with pentane. Yield 110 mg, MP 152-153 °C,

Elemental Analysis for Cu: calcd 8.52; found 8.45; X-ray crystallographic data: space group P-1, Z = 2, a = 12.152 Å, b = 14.099 Å, c = 23.253 Å, α = 90.18°, β = 90.09°, γ = 95.29°, Volume = 3967.0 Å^3.

II. HOMOPOLYMERIZATION AND COPOLYMERIZATION

Reactions were conducted under argon using Schlenk and glovebox techniques. All solvents and monomers were purified by standard techniques, Perrin, D. D., Armarego, W. L F. *Purification of Laboratory Chemicals*; Pergamon: New York, 1988. 30% MAO in toluene, available from Albemarle, Inc. (Baton Rouge, La.), was used as received. General procedure for polymer workup: First a sufficient amount of methanol is added in order to quench the polymerization reaction. Then the mixture is added to 5 to 10 times its volume of methanol containing 10 ppm of 2,6 Di-*tert*butyl-4-methylphenol, (BHT), in order to precipitate the polymer. Then 10 ml of 2 N HCl is added to the mixture containing the polymer and is soaked for a sufficient time to remove the catalyst and cocatalyst from the polymer. The polymer is generally collected by filtration and dried under vacuum. "RT" means ambient or room temperature, i.e. a temperature from about 20 °C to 26 °C.

Example 8 - Polyethylene

A glass lined Parr reactor was loaded in an Ar glove box with 14.1 mg (0.024 mmol) of Cu (diEtBBIL)Cl_2 followed by 30 mL of toluene to give a pale yellow partially dissolved solution. Next 2.0 mL of 30% MAO was added to give a nearly colorless solution. The Parr was sealed and taken to a hood containing the controller for the Parr and pressurized with 270 psig ethylene and polymerized at 80°C for ~24 hours. The reaction was cooled, vented and quenched with MeOH. The product was collected by filtration, washed with MeOH and dried at 70 °C for 2 hours. Yield = 16.15 g of white polymer. Turnover Number (TON), moles substrate converted/moles catalyst = 24,000. ^{13}C NMR (TCE, $Cr(AcAc)_3$) δ 29.5(s,–CH_2–). There were no detectable resonances for branching elsewhere in the spectrum, using the method of Randall, J. Macromol.Sci., Rev. Macromol. Chem. Phys. C29 (292) 1989. (Branch content < 0.5 branches/1000 carbon atoms.) The ^{1}H NMR (TCE) δ

1.3 (s,–CH_2–)δ 0.95 (m, CH_3 end groups) (δ 4.95 - 5.10 (m, olefin end groups). The ratio of CH_3 to olefin end groups was > 3:1. Polymer M_n = 4,900, Mw=13,900, by GPC (in TCB); Tm=139.1 °C, ΔH=209.8 J/g.

Example 9 - Polyethylene Polymerization, Hexane Slurry Conditions

Polymerization was run using a hexane slurry prepared by suspending 3.72 mg (0.0082 mmol) of $Cu(MeBBIOMe)Cl_2$ in hexane followed by activation with 2.5 mL of 10% MAO (0.004 mol). The reactor was pressurized with 125 psig of ethylene and heated to 60 °C for 0.5 h to yield 2.4 g of solid polyethylene (TON=10,900). Polyethylene Mn = 150700, MWD = 2.33 by GPC (in TCE, polyethylene standard). Polymer T_m = 140°C.

Example 10 - Polyethylene Polymerization, moderate Pressure Conditions

A high-pressure HASTELLOY™ reactor was loaded in an Ar glovebox with a slurry prepared by suspending 35 mg (0.077 mmol) of $Cu(MeBBIOMe)Cl_2$ in 4.0 mL of toluene followed by activation with 1.0 ml of 30% MAO (0.005 mol). The reactor was pressurized with 5.6 g (0.20 mol) of ethylene and heated to 80.5 °C, resulting in a pressure of 5170 psig. The pressure dropped to 4390 psig over a 2.75 h period indicating an uptake of ethylene. The polymerization mixture was cooled and quenched with methanol to give 1.1 g of solid polyethylene. (20% yield based on ethylene) Polyethylene Mn = 145,400, MWD = 2.55, Tm = 139 °C, ΔH_f = 122 J/g.

Example 11 - Polymerization of ethylene

The polymerization was run using a slurry prepared by suspending 12.8 mg (0.022 mmol) of $Cu(diEtBBIL)Cl_2$ in 30 mL of toluene and 10 mL of 1,2-dichlorobenzene followed by activation with 2.5 ml of 30% MAO to give a yellow suspension. The Parr reactor was pressurized with 500 psig of ethylene and heated to 80 °C and maintained at 80 °C for 1/2 h during which the pressure dropped from 730 psi to 580

psig. The polymerization mixture was cooled and quenched with methanol to give 7.97 g of solid polyethylene upon workup (TON = 12,700 moles^{PE}/moles catalyst).

Example 12 - Polyethylene Polymerization, Toluene Slurry

The polymerization was run using a toluene slurry prepared by suspending 20.8 mg (0.029 mmol) of [3,3'(1-ethylbenzimidazol-2yl)pentane]copper(II) ditrifluoromethyl-sulfonate, Cu(tetEtBBIM)(trif)$_2$ in 30 mL of toluene followed by activation with 2.0 mL of 30% MAO (0.01 mol) to give a yellow suspension. The PARR™ reactor was pressurized with 300 psig of ethylene and heated to 90° C and further pressurized to 750 psig and maintained at 90 °C for 20 h during which the pressure dropped to 740 psi. The polymerization mixture was cooled and quenched with methanol to give 210 mg of solid polyethylene upon workup. Polyethylene Tm = 137° C.

Example 13 - Copolymerization of ethylene and 1-hexene

A high-pressure HASTELLOY™ reactor was loaded in an Ar glovebox with a slurry prepared by suspending 30.1 mg (0.066 mmol) of Cu(MeBBIOMe)Cl$_2$ in 2.0 mL of toluene followed by activation with 1.0 mL of 30% MAO (0.005 mol). This was followed by the addition of 0.67 g of 1-hexene. The reactor was pressurized with 4.1 g of ethylene (0.146 mol) and heated to 80 °C resulting in a pressure of 850 psig. The pressure dropped to 690 psig over a 1.5 h period and the polymerization mixture was cooled and quenched with methanol to give 1.6 g of solid copolymer. (33.5% yield based on charge of monomers) Copolymer Mn=133,500, MWD = 2.51, Tm = 107, 123 °C.

Example 14 - Poly(*t*-butyl acrylate)

A 20.1 mg (0.044 mmol) quantity of Cu(MeBBIOMe)Cl$_2$ was added to a 100 mL round-bottomed flask in an Ar glovebox. A 10 mL quantity of toluene was added to the flask, followed by 0.11 g of 30 wt. % MAO (0.57 mmol) resulting in an yellow slurry. 7.45 g of *t*-butyl acrylate (freshly distilled from CaCl$_2$ and stabilized with 300 ppm of phenathiazine) was added to the slurry. The flask was covered with

aluminum foil and the mixture was allowed to stir at room temperature for 18 hours in the dark. At the end of this time period, the reaction was quenched with 5 mL of methanol and then the polymer was precipitated out in 150 mL of acidic methanol (10%). The polymer was isolated by filtration and dried under vacuum at 40°C for a day. Yield : 57%. M_n = 470,000; M_w = 851,000; MWD = 1.8. ^{13}C NMR (ppm, $CDCl_3$): 28.2 (s, $-CH_2-CH(COOC(\underline{C}H_3)_3)-$), 34.3-37.6 (m, $-\underline{C}H_2-CH(COOC(CH_3)_3)-$), 42-43.5 (m, $-CH_2-\underline{C}H(COOC(CH_3)_3)-$), 80.5 (m, $-CH_2-CH(COO\underline{C}(CH_3)_3)-$), 173.2-174.1 (m, $-CH_2-CH(\underline{C}OOC(CH_3)_3)-$), 38%rr, 46% mr, 16% mm (by integration of methine peak).

Example 15 - Poly(methyl methacrylate)

19.6 mg of $Cu(MeBBIOMe)Cl_2$ was added to 5 mL of toluene in a 100 mL round-bottomed flask in an Ar glovebox. To another 5 mL quantity of toluene, 4.41 g of methyl methacrylate (stabilized with 400 ppm of phenathiazine) was added, followed by 0.15 g of 30 wt. % MAO (0.78 mmol). This pale yellow solution was added to the flask, which was sealed and covered with aluminum foil. The reaction mixture was stirred at room temperature for 16 hours in the dark. At the end of this time period, the green-yellow reaction mixture was quenched with methanol and then the polymer was precipitated out in 150 mL of acidic methanol (10%). The polymer was isolated by filtration and dried under vacuum at 50°C for a day. Yield : 51%. M_n = 140,000; M_w = 635,000; MWD = 4.6. ^1H NMR (ppm, $CDCl_3$): 0.86, 1.02, and 1.21 (s, $-CH_2-C(C\underline{H}_3)(COOCH_3)-$), 1.5-2.2 (broad m) and 1.91 (s, $-C\underline{H}_2-C(CH_3)(COOCH_3)-$), 3.63 (s, $-CH_2-C(CH_3)(COOC\underline{H}_3)-$), 76% rr, 18% mr, 6% mm (by integration of methyl peaks at 0.8 (rr), 1.0 (mr), 1.2 (mm) ppm).

Example 16 - Poly *n*-butyl vinyl ether

In an Ar glovebox a yellow suspension was prepared by adding 1.0 ml of 30% MAO to 25 ml of toluene containing 10.2 mg (0.022 mmol) of $Cu(MeBBIOMe)Cl_2$. Then 5.0 mL *n*-butyl vinyl ether (44 mmol) was added to the suspension. The mixture was allowed to stir at RT for 20 h during which time the mixture became a viscous pale red-brown solution. The polymerization was quenched with methanol. Upon workup

2.07 g of amorphous poly *n*-butyl vinyl ether was obtained Yield : 53%, IR (film, KBr plate, cm^{-1}) 2956 (s), 2930 (s), 2871 (s), 1464 (m), 1457 (m), 1377 (m), 1039 (s). ^1H NMR ($CDCl_3$)δ 0.95 (t,CH_3), 1.3-1.9(m,CH_2), 3.3-4.7(m, CH–o,–O–Ch_2); ratio δ 0.95-1.9/δ 3.3-4.7 = 3H/9H. ^{13}C NMR ($CDCl_3$)δ 13.5 (s, CH_3), 19.5(s,$CH_2$0,31.0(s,CH_2)39.0-41.0(m,CH_2), 67.5(m,–OCH), 73.5(m,–OCH_2). GPC: Mn=6300, M_2=30,000.

<u>Example 17</u> - Ethylene/*t*-Butyl Acrylate Copolymer

A Parr reactor was loaded with 33.5 mg (0.0679 mmol) of Cu (tet EtBBIM)Cl_2 followed by 35 mL of toluene, then by 2.0 mL of 30% MAO (.01 moles) in an argon dry box to give a yellow suspension. The 6.0 mL (5.37g) (54 mmol) of *t*-butyl acrylate was added to give a yellow-green suspension. The Parr was sealed and set up in a hood and pressurized with 750 psig of ethylene and polymerized at 90°C for 24 hours. The reaction mixture was cooled and quenched with MeOH. Subsequently, the contents of the reactor were added to <u>ca</u> 150 mL of MeOH giving a white precipitate. A 10 mg quantity of BHT and 25 mL of HCl were added, and the mixture was allowed to soak to dissolve catalyst residues. The polymer was extracted from the water phase with CH_2Cl_2 and Et_2O The solvents were removed by vacuum and the polymer was dried in a vacuum oven at 55°C to give 2.96 g of pale-green solid. Catalyst turnovers (TON) (moles substrate converted per mole of catalyst) for t-butyl acrylate is 307, for ethylene is 151.

^1HNMR ($CDCl_3$)δ 0.7-0.85 (m CH_3 end groups), δ 1.1-1.25 (m –CH_2–), δ 1.4 (s –O–C(CH_3)$_3$)), δ 2.05-2.25 (broad m, —CH—). The presence of a multiplet rather than a triplet at 2.05 - 2.25 ppm, and the lack of a resonance at 1.6 ppm is consistent with in chain ester units rather than ester ended branches, such as –$(CH_2)_nCH_2COOC(CH_3)_3$. Integration of the monomer units indicates a copolymer composition of <u>ca</u> 67% t-butyl acrylate units and 33% ethylene units. ^{13}C NMR (δ, $CDCl_3$), δ 27 ppm (t, CH_3's of the t-butyl group), δ 67 (s, —C— of t-butyl group), δ 41.5-42.8 (m, –CH_2–), δ 43.8-44.8 (m, –CH_2–), δ 46.5 (s, –CH–). Branching analysis of CH_3 (at δ 19.8), Et (at δ 11.6), C_3-C_6 (at δ 14.1) by ^{13}C NMR gave ≤ 4.4

CH_3 branches/1000 C atoms, 7.7 CH_3CH_2 branches/1000 C atoms, and 5.1 propyl to hexyl branches/1000 carbon atoms. GPC (THF, polystyrene calibration, with DRI and UV detection at 215 nm) of a sample purified through a neutral alumina column to remove MAO and unreacted monomer: Mn = 26,200, Mw = 34,200. The presence of UV activity across the molecular weight distribution is an indication of copolymer formation. DSC (Tg = +4 and no Tm) also confirms copolymer rather than homopolymers.

Comparative Example 1

A copolymer was prepared following the procedure of Examples 134 of PCT WO96/23010. ^{1}HNMR ($CDCl_3$): 2.2(t, $-CH_2CO_2C(CH_3)_3$, ester ended branches), 1.6 (m, $CH_2CH_2CO_2C(CH_3)_3$, ester ended branches), 1.45 (s, $-C(CH_3)_3$), 0.95-1.45, (m, CH, and other CH_2). 0.75-0.95 (m, CH_3, ends of hydrocarbon branches or ends of chains). This spectrum shows that the esters are primarily located at the ends of hydrocarbon branches; integration gave 6.7 mole% *t*-butyl acrylate. ^{13}CNMR quantitative analysis, branching per 1000 CH_2: Total methyls (74.8); methyl (27.7), Ethyl (15.3), propyl 1.5), butyl (8.6), ≥ amyl and end of chains (30.8), $-CO_2C(CH_3)_3$ ester (43.2). Ester branches $-CH(CH_2)_nCO_2C(CH_3)_3$ as a % of total ester: n ≥ 5 (44.3), n = 1, 2, 3, 4 (37.2), n = 0 (18.5). GPC (THF, PMMA standard): Mn=6000 Mw=8310 Mw/Mn=1.39.

Example 18 - Ethylene/MMA Copolymer

In an Ar glovebox, a Parr reactor was loaded with 26.1 mg (.055 mmol) or orange Cu (BBIK) Cl_2, followed by 30 mL of toluene, and finally with 2.0 mL of 30% MAO (.010 mol). Then 4.0 mL (3.74g) (0.0374 mmol) of methyl methacrylate, containing 400 ppm of phenathiazine, was added. The Parr reactor was sealed and set up in a hood and pressurized with 750 psig of ethylene and polymerized at 90°C for 19.5 hours. The reaction was quenched with MeOH. The polymer was collected by filtration to give 0.68 g of white polymer. Turnover Number (TON) (moles substrate converted for mole of catalyst) for MMA = 109, for ethylene = 50.

IR (film, cm^{-1}) 3441 w, 3001 s, 2951 s, 2943 sh, 1736 s (ester C=O), 1456 (CH_2), 1246 s (C-O), 1149 s (C-O), 1000 sh, 991 s, 914 w, 844 m, 812 w, 756 m (CH_2). ^1H NMR ($CDCl_3$) δ 0.61(m, CH_3 end groups) δ, 0.85 - 1.1 (m, CH_3). δ 1.45-2.45 (m, $-CH_2-$), δ 3.25-3.35 (s, $-OCH_3$). Integration of ^1H NMR indicates a copolymer composition of 71.3% MMA and 28.7% ethylene. GPC (in TCB, polystyrene calibration): Mn = 1,150, Mw = 35,900; Tg of polymer - 61.2°C (first heat), no Tm; ^{13}C NMR ($CDCl_3$), δ 18-22 (m, $-CH_2-$), δ 31-32, δ 40-41 (m, $-CH_2-$), 45.5-46.5 (m, —C— δ 52.5 (s, $-OCH_3$), δ 55.8 (m, $-CH_2-$). No backbone methine carbons were found by a DEPT (Distortionless Enhancement by Polarization Transfer) experiment, indicating no detectable backbone branch sites.

Example 19 - Ethylene/*n*-Butyl Vinyl Ether Copolymer

A Parr reactor was loaded with 33.3 mg (0.0673 mmol) of Cu (tetEtBBIM) Cl_2 and 30 mL of toluene, followed by the addition of 2.0 mL of 30% MAO (0.010 mol) to give a yellow suspension. A 5 mL quantity (44 mmol) of *n*-butyl vinyl ether was added with no immediate color change. The Parr reactor was sealed and taken to a hood containing the controllers for the reactor. The reactor was pressurized with 750 psig of ethylene and the mixture was reacted at 60°C for 20 hours. The reaction was cooled, quenched and the product was isolated. The polymer was soaked in MeOH/HCl to remove catalyst residues. The product was washed and dried to yield .420 g of viscous oil. TON (*n*-butyl vinyl ether) = 61; TON (ethylene) = 11.5. IR (film, KBr plate, cm^{-1}) 2958(s), 2931(s)(CH_2), 2872(s), 1465(s), 1458(s), 1377(m), 1093(s), 1039(m), 979(w), 932(w), 913(w), 859(w), 802(m) 737(m) CH_2, ^{13}C NMR ($CDCl_3$ + $CrAcAc)_3$ δ 13.5 (s, CH_3), 19.5 (s, CH_2) 29.5-30.0 (m, $-CH_2-$), 31.0(s,CH_2) 39.0-41.5 (m, CH_2), 68.5(m, –CH–O), 73.5 (m, $-OCH_2$). The presence of the –CH–O resonance at 68.5 ppm indicates an in-chain copolymer. Integration of the NMR indicates a copolymer composition of 84.3% *n*-butyl vinyl ether, and 15.8% ethylene. The polymer Tg = -97, -63°C with no Tm is consistent with copolymer formation. GPC (polystyrene calibration with DRI and UV detection at 215 nm), Mn = 5390, Mw = 23620, Mw/Mn = 4.38. The presence of UV activity across the molecular weight-distribution confirms copolymer formation.

Example 20 - Poly(lauryl acrylate)

In a nitrogen glovebox, a polymerization tube was loaded with 17.9 mg (FW 744.5, 2.4×10^{-5} mole) of Cu(diOctBBIL)Cl_2 catalyst, followed by 20.25 mL of toluene, and finally with 0.8 mL of 10% MAO (0.00138 mole). Then 3.0 g (FW 240.39, 0.0125 mole) of inhibitor free lauryl acrylate was added. The mixture was allowed to stir at room temperature for 24 hours. The yield was 47%, upon workup. ^{13}C NMR of the product showed characteristic polymer ester peak at 174.4 ppm as against to 166.1 peak for monomer ester. IR (film, cm^{-1}) 1736 (polymer ester carbonyl), 1464, 1396, 1377, 1258, 1167 and 721. GPC (solvent: THF, polystyrene calibration) of the product gave Mn 16100 and Mw 69100.

Example 21 - Ethylene/Lauryl Acrylate Copolymer

In a nitrogen glove box, a Parr reactor was loaded with 15.0 mg (FW 744.5, 2.01×10^{-5} mole) of Cu(diOctBBIL)Cl_2 catalyst, followed by 30 mL of toluene, and finally with 2.4 mL of 10% MAO (0.00414 mole). Then 2.0 g (FW 240.39, 0.00832 mole) of inhibitor free lauryl acrylate was added. The Parr reactor was sealed and set up in a hood and pressurized with 700 psig of ethylene and polymerized at 80°C for 48 hours. The polymer was collected by filtration to give 1.3g of product. Turnover number (TON) (moles of substrate converted for mole of catalyst) for LA = 234, for ethylene = 306. The ^{13}C NMR of the product showed peaks due to both ethylene, as well as lauryl acrylate. Integration of the peak indicates a copolymer composition of 56.7 mole % ethylene, and 43.3 mole % lauryl acrylate. GPC (solvent: THF, polystyrene calibration) of the product gave Mw 7700.

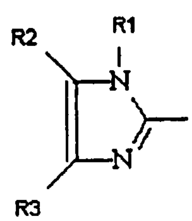
CLAIMS:

1. A catalyst system comprising:

(a) a catalyst having the formula LM X_1X_2 wherein X_1 and X_2 are independently selected from the group consisting of halogens, hydride, triflate, acetate, triflouroacetate, tris perflourotetraphenyl borate, tetraflouro borate, C1 through C12 straight chain or branched alkyl or alkoxy, C3 through C12 cyclo alkyl or cyclo alkoxy, and aryl; M is selected from the group consisting of Cu, Ag, and Au; and L is a nitrogen-containing bidentate ligand,

(b) an activating cocatalyst.

2. The catalyst system of Claim 1 wherein L has the formula [ABA'] or [AA'] wherein A and A' are independently selected from the group consisting of



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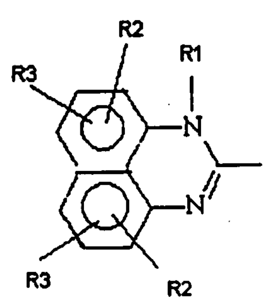

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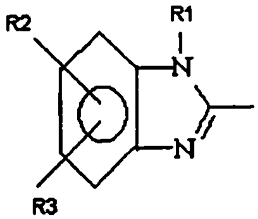

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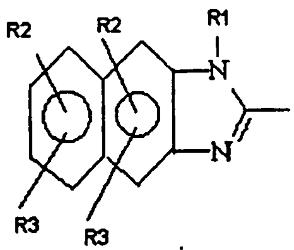


; wherein R1 is independently selected from the group consisting of hydrogen, C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl, aryl, and triflouroethane;

R2 and R3 are independently selected from the group consisting of hydrogen, C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl, C1 through C12 alkoxy, F, Cl, SO_3, C1 through C12 perflouroalkyl, and $N(CH_3)_2$;

B is selected from the group consisting of non-substituted C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl; methoxy; amino; halo; and C1 through C12 haloalkyl substituted straight chain or branched alkyl or cyclo alkyl of up to 12 carbon atoms, or a C1-C40 aryl or alkylaryl group.

3. The catalyst system according to claim 2 wherein L is selected from the group consisting of 1,1'bis(1-methylbenzimidazol-2 yl)1" methoxyethane and 3,3'(1-ethylbenzimidazol-2yl) pentane, and 2,2' bis[2-(1-alkylbenzimidazol-2yl)]biphenyl, where the alkyl group is from C1-C20 atoms.

4. The catalyst system of claim 3 wherein the cocatalyst is selected from the group consisting of alkylalumoxanes, aluminum alkyls, aluminum halides, alkyl aluminum halides, Lewis acids and alkylating agents, and mixtures thereof.

5. The catalyst system of claim 4 wherein the ratio of metal complex to activating cocatalyst is from $1{:}10^{-2}$ to $1{:}10^{6}$.

6. The catalyst system of claim 5 wherein $X_1 = X_2$ and are selected from the group consisting of chloride, bromide, and trifluoromethylsulfonate.

7. A composition have the formula LMX_1X_2 wherein X_1 and X_2 are independently selected from the group consisting of halogens, hydride, triflate, acetate, triflouroacetate, tris perflourotetraphenyl borate, tetraflouro borate, C1 through C12 straight chain or branched alkyl or alkoxy, C3 through C12 cyclo alkyl or cyclo alkoxy, and aryl; M is selected from the group consisting of Cu, Ag, and Au; and L is a nitrogen-containing bidentate ligand.

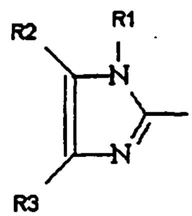
8. The composition of claim 7 wherein L is selected from the group consisting of 1, 1' bis(1-methylbenzimidazol-2 yl)1" methoxyethane and 3,3'(1-ethylbenzimidazol-2yl) pentane, and 2,2'bis[2-(1-alkylbenzimidazole-2yl)]biphenyl. M is copper, and X_1 and X_2 are selected from the group consisting of chlorine and bromine.

9. A method for polymerizing olefinic monomers selected from the group consisting of:

(a) acyclic aliphatic olefins, (b) olefins having a hydrocarbyl polar functionality and (c) mixtures of (i) at least one olefin having a hydrocarbyl functionality (ii) at least one acyclic aliphatic olefin, the method comprising contacting the olefinic monomer or monomers under polymerization conditions with a catalyst system comprising (a) a catalyst having the formula LM X_1X_2, wherein X_1 and X_2 are independently selected from the group consisting of halogens, hydride, triflate, acetate, triflouroacetate, trisperflourotetraphenyl borate, tetraflouro borate, C1 through C12 straight chain or branched alkyl or alkoxy, C3 through C12 cyclo alkyl or cyclo alkoxy, and aryl; M is selected from the group consisting of Cu, Ag, and Au; and L is a nitrogen-containing bidentate ligand,

(b) an activating cocatalyst.

10. The method of claim 9, wherein L has the formula [ABA'] or [AA'] wherein A and A' are independently selected from the group consisting of



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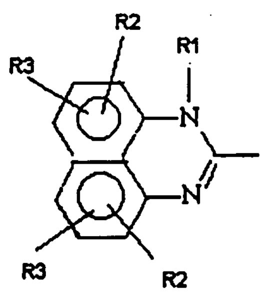

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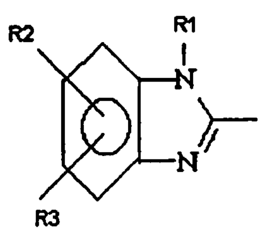

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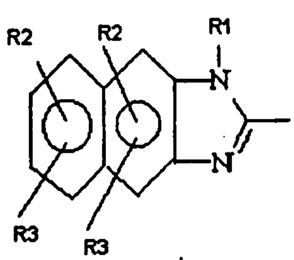

wherein R1 is independently selected from the group consisting of hydrogen, C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl, aryl, and triflouroethane;

R2 and R3 are independently selected from the group consisting of hydrogen, C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl, C1 through C12 alkoxy, F, C1, SO_3, C1 through C12 perflouroalkyl, and $N(CH_3)_2$;

B is selected from the group consisting of non-substituted C1 through C12 straight chain or branched alkyl, C3 through C12 cyclo alkyl; methoxy; amino; halo; and C1 through C12 haloalkyl substituted straight chain or branched alkyl or cyclo alkyl of up to 12 carbon atoms or a C1-C40 aryl or alkylaryl group.

11. The method of claim 10 wherein the cocatalyst is selected from the group consisting of alkylalumoxanes, aluminum alkyls, aluminum halides, alkyl aluminum halides, Lewis acids other than any of the foregoing, alkylating agents and mixtures thereof.

12. The method of claim 11 wherein the contacting is at a temperature in the range of from about -100°C to about 250°C and at pressures of from about 15 psig to about 30,000 psig.

13. The method of claim 12 wherein the contacting is conducted in a solvent.

14. The method of claim 13 wherein the solvent is an aliphatic or aromatic hydrocarbon solvent or a halogenated aromatic solvent, or mixture of thereof.

15. The method of claim 13 wherein the olefinic monomer is selected from the group consisting of (a) acyclic aliphatic olefins, (b) olefins having a hydrocarbyl polar functionality wherein a homopolymer is formed.

16. The method of claim 13 wherein the olefinic monomer is selected from mixtures of (i) at least one olefin having a hydrocarbyl functionality and (ii) at least one acyclic aliphatic olefin, whereby a copolymer is formed.

17. A substantially linear copolymer having a polymer chain with the formula:

$$-\left(A\right)_{1-y}\left(CH_2-\underset{\displaystyle X}{\overset{|}{C}}R\right)_y$$

where A is a segment derived from an acyclic aliphatic olefin of 2 to about 20 carbon atoms;

R is H or CH_3;

X is - OR^1 or - $COOR^1$;

R^1 is an alkyl group of 1 to about 24 carbon atoms; and

Y is from about 0.02 to about 0.95 and wherein the $-\left(CH_2-\underset{\displaystyle X}{\overset{|}{C}}R\right)-$ group is substantially in the polymer chain.

18. The copolymer of claim 16 wherein A is a segment derived from ethylene, such that it has less than about 20 branches/1000 carbon atoms.

19. A copolymer having a polymer chain represented by the formula:

$$-\left(A\right)_{1-y}\left(CH_2-\underset{\displaystyle X}{\overset{|}{C}}R\right)_y$$

where A is a segment derived from an acyclic aliphatic olefin of 2 to about 20 carbon atoms;
R is H or CH_3;
X is -OR^1 or –$COOR^1$;
R_1 is an alkyl group of 1 to about 24 carbon atoms and Y is from 0.18 to 0.85.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/26657

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 31/00
US CL : 502/155, 165, 167
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/155, 165, 167

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,954,664 A (NAPIER et al) 4 May 1976, col. 3, l. 26-60.	1
X	US 5,369,073 A (SOMMAZZI et al) 29 November 1994, col. 2, l. 8 to col. 3, l. 39, examples.	1
X	JP 54-39032 A (MITSUI) 24 March 1979, abstract.	1
X	JP 56-22751 A (SUMITOMO) 3 March 1981, abstract.	1
X	JP 57-38733 A (KURARAY) 3 March 1982, abstract.	1
X	JP 63-159362 A (MITSUBISHI) 2 July 1988, abstract.	1

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"B" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 MARCH 1999	12 APR 1999

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	JAMES PASTERCZYK
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/26657

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 49-48433 A (SANKYO CO LTD) 21 December 1974, see abstract.	1-6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/26657

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-6

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-6, drawn to a catalyst system.
Group II, claim(s) 7-8, drawn to a particular compound.
Group III, claim(s) 9-16, drawn to a method of polymerizing olefins.
Group IV, claims 17-19, drawn to olefin copolymers.

The inventions listed as Groups I-IV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the catalyst of group I is known (see JP-A-49-48433).